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<b>(54) Title:</b> AN IMPROVED PROCESS FOR SINTERING ALUMINUM NITRIDE TO A HIGH THERMAL CONDUCTIVITY AND RESULTANT SINTERED BODIES  <b>(57) Abstract</b>  Sintered aluminum nitride bodies having a TC of at least 200 W/m.K are prepared by sintering under non-reducing conditions and controlling interrelated parameters such as binder burnout atmosphere, heating rate, sintering temperature, time at sintering temperature, cooling rate and cooling temperature. The sintered bodies may also have a TC in excess of 270 W/m.K.		

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AN IMPROVED PROCESS FOR SINTERING ALUMINUM NITRIDE TO A HIGH THERMAL  
CONDUCTIVITY AND RESULTANT SINTERED BODIES

TECHNICAL FIELD

The present invention relates generally to a process for preparing sintered  
5 aluminum nitride (AlN) bodies and to bodies resulting from the process. The present invention  
relates more particularly to a process for preparing sintered AlN bodies having a thermal  
conductivity (TC) in excess of 270 watts/meter<sup>°K</sup> (W/m<sup>°K</sup>).

BACKGROUND OF THE INVENTION

AlN is subject to increasing interest as a microelectronic substrate material. With  
10 a TC approaching that of berylia (BeO) and a thermal expansion coefficient well matched to  
silicon, AlN represents an attractive alternative in high power or multi-chip module  
applications.

At room temperature, single crystal AlN has a theoretical TC of 319 W/m<sup>°K</sup>.  
Polycrystalline ceramics tend to have a lower TC than single crystal AlN due to a number of  
15 factors. The factors include random orientation of AlN grains, crystalline lattice impurity levels  
and existence of crystalline grain boundary phases with an even lower TC.

F. Miyashiro et al., in "High Thermal Conductivity Aluminum Nitride Ceramic  
Substrates and Packages", IEEE Transactions on Components, Hybrids, and Manufacturing  
Technology, Vol. 13, No. 2, 313-19 (June 1990), suggest that three key technologies are very  
20 important if one is to realize the highest TC by sintering. The technologies are: reducing or  
minimizing oxygen content of AlN powders; proper choice and quantity of additives; and  
sintering conditions in terms of temperature, time and atmosphere. They suggest that a  
reducing atmosphere yields the highest TC.

H. Buhr et al., in "Phase Composition, Oxygen Content, and Thermal Conductivity  
25 of AlN(Y<sub>2</sub>O<sub>3</sub>) Ceramics", J. Am. Ceram. Soc. 74[4], 718-723 (1991), disclose sintering cold  
isostatically pressed cylindrical compacts under a pressure of 0.2 MPa nitrogen. They employ  
heating rates of 16 to 30 K per minute (K/min).

K. Watari et al., in "Sintering Chemical Reactions to Increase Thermal Conductivity  
of Aluminum Nitride", J. Mater. Sci. 26, 4727-32 (1991), discuss chemical reactions to increase TC  
30 by decreasing oxygen contents during AlN sintering with an Y<sub>2</sub>O<sub>3</sub> additive in a reducing  
nitrogen atmosphere with carbon. They use a heating rate of 15 K/min and report TC values as  
high as 220 W/m<sup>°K</sup>.

T. A. Guiton et al., in "Optimization of Aluminum Nitride Thermal Conductivity  
Via Controlled Powder Processing", Mat. Res. Soc. Symp. Proc., Vol 271, 851-56 (1992), suggest  
35 that TC depends strongly on oxygen chemistry and sintering parameters. They disclose two sets  
of sintering parameters, denominated as "Cycle 1" and "Cycle 2" in Table II (page 852). Cycle 2  
includes a heating rate of 2.5°C/min, a sintering temperature of 1850°C, a sintering time of 3  
hours, a cooling rate of 1°C/min and a cooling temperature of 1500°C.

US-A 4,847,221 discloses a process for preparing sintered AlN bodies as well as the resultant bodies. The process comprises firing an admixture of AlN powder and one or more rare earth compounds in an amount of 0.01 to 15 wt-% in a reducing atmosphere at a temperature of 1550°C to 2050°C for four hours or more. The resultant bodies have a TC as high as 272 W/m-K.

US-A 4,778,778 reports a particular sintering cycle described in a copending application. The cycle includes: increasing the temperature of a compacted AlN body from room temperature to a sintering temperature at a rate of no more than 250°C per hour (°C/hr); sintering the body in an inert atmosphere at a temperature of 1600°C to 1900°C; and cooling the sintered body at a rate of no more than 300°C/hr. The '778 patent improves upon this cycle by introducing an amount of hydrogen gas along with the inert gas up to a temperature of 1200°C, after which pure inert gas is introduced.

#### Summary of the Invention

One aspect of the present invention is a sintered polycrystalline AlN ceramic body having a TC at room temperature (25°C) of  $> 270 \text{ W/m}^{\circ}\text{K}$ .

A second aspect of the present invention is an improved process for preparing a sintered polycrystalline AlN body having a TC of greater than 200 W/m<sup>°</sup>K by heating an admixture of AlN powder and at least one powdered sintering aid in the presence of nitrogen gas to a sintering temperature, holding the admixture at that temperature for a period of time sufficient to convert the admixture to a sintered body, and thereafter cooling the body to ambient temperature, characterized by a combination of heating to the sintering temperature at a rate of from  $> 0^{\circ}\text{C/min}$  to  $6^{\circ}\text{C/min}$ , maintaining that temperature for a period of time sufficient to convert the admixture to a sintered body having a density of  $> 95\%$  of theoretical density, and cooling the sintered body in the presence of a vacuum or an inert gas from the sintering temperature to a temperature of 1400°C at a rate of from  $> 0^{\circ}\text{C/min}$  to  $6^{\circ}\text{C/min}$  before cooling the sintered body further to ambient temperature (25°C).

A third aspect of the present invention centers upon the sintered body resulting from the process of the second aspect.

#### Description of Preferred Embodiments

AlN powder suitable for purposes of the present invention may be of commercial or technical grade. It should not contain any impurities that would have a significant adverse effect upon desired properties of a resulting sintered product. Although some level of impurities is present in commercial powders, that level should be less than that which produces the aforementioned adverse effect.

The AlN powder typically has a bound oxygen content of  $< 4 \text{ wt}\%$ . The oxygen content is desirably  $< 3 \text{ wt}\%$  and preferably  $< 2 \text{ wt}\%$ .

The AlN powder also typically has a surface area (SA), measured by conventional B.E.T. absorption methods, of from 1.5 to 10 square meters per gram ( $\text{m}^2/\text{g}$ ). The powder SA is desirably from 2 to 9  $\text{m}^2/\text{g}$ .

AlN powder meeting these specifications is preferably prepared either by  
5 carbothermal reduction of alumina ( $\text{Al}_2\text{O}_3$ ) or direct nitridation of aluminum metal. AlN powders may also be prepared by other processes using aluminum alkyls or aluminum halides. Preferred carbothermal AlN powders are available from The Dow Chemical Company under the trade designation XUS 35544 and XUS 35548 or Tokuyama Soda under the trade designations Grade F and Grade H. Mixtures of these and other powders may also be used.

10 The AlN powder may be mixed with any of the art-recognized sintering aids such as, for example, oxides or fluorides of metals selected from: yttrium; rare earth metals such as lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, and dysprosium; and alkaline earth metals such as calcium, strontium and barium. A combination of sintering aids may be used in place of a single sintering aid. Yttrium compounds, particularly yttria ( $\text{Y}_2\text{O}_3$ ),  
15 yield satisfactory results.

The sintering aid or combination of sintering aids is suitably admixed with AlN powder in an amount of from 0.05 to 10 wt%, based upon combined weight of sintering aid and AlN powder. The amount is desirably from 0.05 to 3 wt%. The sintering aid preferably has a SA similar to that of the AlN powder.

20 Preparing an admixture of AlN powder and the sintering aid(s) may be carried out by conventional procedures such as attritor milling and wet and dry ball milling. Wet ball milling with an appropriate solvent and suitable milling media provides satisfactory results. Milling media, usually in the form of cylinders or balls, should have no significant adverse effect upon admixture components or upon sintered bodies prepared from the admixture. A liquid  
25 milling or mixing medium such as ethanol, heptane or another organic liquid may be used. After mixing, the milling medium may be removed by conventional procedures to yield an admixture suitable for conversion to ceramic greenware. Oven drying and spray drying produce satisfactory results.

An organic binder may also be used during processing of the admixture into a  
30 sintered body. Suitable binders are well known in the art and typically comprise high molecular weight organic materials that are soluble in organic solvents. Illustrative binders include polyethyloxazoline, industrial waxes such as paraffin, highly viscous polyglycols, polymethylmethacrylate and polyvinyl butyral. Polyethyloxazoline is particularly suitable. The binder is suitably added to admixture components prior to milling.

35 Ceramic greenware may be prepared by any one of several conventional procedures such as extrusion, injection molding, die pressing, isostatic pressing, slip casting, roll compaction or forming or tape casting to produce a desired shape. Particularly satisfactory results are obtained by dry pressing a spray dried admixture or tape casting a slurry.

The ceramic greenware is desirably subjected to conditions sufficient to remove the organic binder prior to sintering. Binder removal, also known as binder burn out, typically occurs by heating the greenware to a temperature that ranges from 50 to 1000°C to pyrolyze, or thermally decompose, the binder. The temperature varies depending upon the binder.

- 5 Thermal decomposition may be carried out at or near ambient pressure or in a vacuum. It may be carried out in the presence of atmospheric air or in a nonoxidizing atmosphere that is desirably established with an inert gas. The inert gas is suitably nitrogen, a source of nitrogen such as ammonia, or a noble gas such as argon. The inert gas is preferably nitrogen. As a general rule, binder burn out in the presence of an inert gas yields a higher residual carbon  
10 level than binder burn out in the presence of atmospheric air. Binder burnout in the presence of nitrogen is preferred for purposes of the present invention.

- Sintered polycrystalline AlN bodies having a TC of  $> 200 \text{ W/m}^{\circ}\text{K}$  are suitably prepared under nonoxidizing conditions by combining several, interrelated sintering parameters. The parameters are heating rate, sintering temperature, time at sintering  
15 temperature, cooling rate, cooling temperature, cooling environment and type and amount of sintering aid.

- Sintering of the greenware occurs in the presence of gaseous nitrogen or a source of gaseous nitrogen and is followed by cooling in a nonreducing environment. The latter may be established by using either an inert gas or a vacuum. The inert gases described as suitable  
20 for binder burn out are also suitable for use in this aspect of the process. One means of establishing a nonreducing environment, at least in part, includes placing the greenware into a crucible fabricated from a nonreducing material prior to sintering and cooling. The non-reducing material is desirably selected from boron nitride (BN), AlN, molybdenum metal, and tungsten metal. BN and AlN are preferred nonreducing materials for a graphite furnace.  
25 Molybdenum metal or tungsten metal are preferred nonreducing materials for a tungsten furnace.

- Because the parameters of heating rate, cooling rate, sintering temperature, time at sintering temperature, cooling temperature and amount and type of sintering aid are closely interrelated, several, but not all, parameter combinations lead to a TC of  $200 \text{ W/m}^{\circ}\text{K}$  or more.  
30 As an additional consideration, a given combination of parameters may produce such a TC in one AlN powder but not in another. This disparity stems from variations in powder properties, particularly impurity levels, and in methods of synthesizing powders as in carbothermal synthesis versus direct nitridation. As a further consideration, differences in binder burn out atmosphere lead to modifications of desirable parameter combinations.

- 35 Using a single AlN powder as an example, various parameter combinations for nitrogen binder burn out (BBO) and air BBO that produce a TC  $\geq 200 \text{ W/m}^{\circ}\text{K}$  or more using 3 wt%  $\text{Y}_2\text{O}_3$  as a sintering aid are shown in Table I. The AlN powder is commercially available from The Dow Chemical Company under the trade designation XUS 35548 and has the

following specification: an oxygen content of  $0.8 \pm 0.2$  wt%; a carbon content  $\leq 0.08$  wt%; a silicon content  $\leq 100$  parts per million (ppm); a calcium content  $\leq 200$  ppm; an iron content  $\leq 35$  ppm; and a SA of  $2.8 \pm 0.2$  m<sup>2</sup>/g.

Parameter combinations for nitrogen BBO that produce a TC  $\geq 270$  W/m<sup>2</sup>K using the same AlN powder and either 2 or 3 wt% Y<sub>2</sub>O<sub>3</sub> as a sintering aid are shown in Table II. The amount of Y<sub>2</sub>O<sub>3</sub> varies in direct proportion to the AlN powder's oxygen content. In other words, with an oxygen content at or near 0.6 wt%, 2 wt% Y<sub>2</sub>O<sub>3</sub> suffices whereas an oxygen content at or near 1 wt% requires as much as 3 wt% Y<sub>2</sub>O<sub>3</sub>. The actual level of sintering aid is tied, at least in part, to residual carbon levels and may be readily determined without undue experimentation.

Table I

Condi- tion	BBO Atmos- phere	Sinter Temp (°C)	Sinter Time (min.)	Heat Rate (°C/min)	Cool Rate (°C/min)
1	N <sub>2</sub>	1817	165	$\leq 1.2$	$\leq 5.4$
2	N <sub>2</sub>	1817	165	$\leq 0.6$	$\leq 5.4$
3	N <sub>2</sub>	1817	165	$\leq 5.4$	0.1
4	N <sub>2</sub>	1817	165	$\leq 5.4$	$\leq 1.1$
5	N <sub>2</sub>	1817	$\leq 278$	$\leq 5.4$	0.1
6	N <sub>2</sub>	1862	165	$\leq 5.4$	$\leq 5.5$
7	N <sub>2</sub>	1908	238	$\leq 2.3$	$\leq 5.5$
8	N <sub>2</sub>	1908	238	$\leq 1.6$	$\leq 5.5$
9	N <sub>2</sub>	1908	$\geq 133$	1.6	$\leq 5.5$
10	N <sub>2</sub>	1908	165	$\leq 5.4$	$\leq 0.5$
11	N <sub>2</sub>	1908	165	3	$\leq 1.1$
12	N <sub>2</sub>	1908	165	0.6	$\leq 5.5$
13	Air	1862	165	$\leq 1.3$	0.1
14	Air	1862	165	$\leq 0.8$	$\leq 0.5$
15	Air	1862	165	$\leq 0.6$	$\leq 0.5$

Table II

Condi- tion	Sinter Temp (°C)	Sinter Time (min.)	Heat Rate (°C/min)	Cool Rate (°C/min)	Cool- ing Temp (°C)
1	1850-1875	80-180	0.6	0.1	$\leq 1650$
2	1850-1875	80-180	0.6	$\leq 0.2$	$\leq 1275$
3	1850-1875	80-180	0.8	0.1	$\leq 1275$
4	1850-1875	80-180	$\leq 1.4$	0.1	1160
5	1850-1875	80-180	$\leq 1.7$	0.1	1160
6	1850-1875	80-180	0.6	$\leq 0.6$	1160
7	1850-1875	80-180	0.6	$\leq 0.4$	1160
8	1850-1875	80-180	$\leq 1$	0.4	1160
9	1863	165	$\leq 3$	0.1	$\leq 1400$

The combinations shown in Tables I and II are particularly suitable when the powder is XUS 35548 (The Dow Chemical Company). Some modification of the combinations may be needed depending upon factors such as oxygen content of the AlN powder, residual carbon content of the AlN greenware and amount and type of sintering aid present in the greenware. If, for example, the powder has an oxygen content at or near the upper limit of the specification and the amount of  $Y_2O_3$  is 3 wt% in Table I or 2 wt% in Table II, modification may be necessary only for condition 9 of Table II. As another example, modification of conditions 1, 7, 9, 11 and 14 of Table I may also be necessary when such a powder is used in combination with a lesser amount, such as 2 wt%, of  $Y_2O_3$ . The modification, particularly with respect to Table I, may be as simple as lowering the upper limit of the cooling rate by  $< 1^\circ\text{C}/\text{min}$ . If the same powder has an oxygen content at or near the lower limit of the specification, the lesser amount of  $Y_2O_3$  may be used with little or no modification of the combinations shown in Tables I and II. Further modifications may be made without undue experimentation.

The combinations shown in Tables I and II generally suffice to yield a sintered body having a density of  $> 95\%$  of theoretical density. The density is desirably  $\geq 97.5\%$ , preferably  $\geq 99\%$  and more preferably  $\geq 99.5\%$  of theoretical density.

Sintered AlN bodies prepared under nonreducing conditions in accordance with the process of the present invention have a TC of  $\geq 200 \text{ W/m}\cdot\text{K}$ . The TC is desirably  $\geq 240 \text{ W/m}\cdot\text{K}$ , preferably  $\geq 270 \text{ W/m}\cdot\text{K}$ , more preferably  $\geq 274 \text{ W/m}\cdot\text{K}$ . The TC is also desirably  $\leq 319 \text{ W/m}\cdot\text{K}$ . A TC of  $\leq 285 \text{ W/m}\cdot\text{K}$  is readily attainable.



Sintered AlN bodies prepared as described herein also display color/translucency combinations that range from light cream and translucent to dark gray or even black and opaque. Surface appearance, also known as mottling (marked with spots or blotches of different color or shades of color as if stained), varies from a high degree of mottling to an absence of visually detectable mottling. Skilled artisans can attain a desired combination of color, degree of mottling and TC without undue experimentation.

The following example is solely for purposes of illustration and is not to be construed, by implication or otherwise, as limiting the scope of the present invention.

Example

Ceramic greenware was prepared from admixtures of 2000 g quantities of various AlN powders, either 2 or 3 wt% (41 g or 62 g) Y<sub>2</sub>O<sub>3</sub> (Molycorp, 99.99% purity) and 6.7 wt% (134.2 g) of a binder composition. The binder composition was a 33/67 weight ratio blend of polyethyloxazoline and polyethylene glycol 3350 (The Dow Chemical Company). The binder was dissolved in 3000 g of ethanol after which the AlN and Y<sub>2</sub>O<sub>3</sub> powders were added. The admixtures were ball milled for five hours. The solvent was removed by spray drying.

Table III. Powder Data

Powder ID	O (wt %)	C (wt %)	Si (ppm)	Ca (ppm)	Fe (ppm)	S.A. (m <sup>2</sup> /g)
A	0.63	0.03	77	158	17	2.75
B	1.04	0.05	74	107	17	2.86
C	1.19	0.05	94	189	28	3.33
D	1.25	0.04	<20	84	<10	3.67
E	0.91	0.03	36	220	<10	2.72

The dried powders were dry pressed into greenware using a 7/8 inch (2.2 cm) round die under uniaxial pressure at 6.9 megapascals (MPa). The binder composition was removed from the greenware in the presence of either air (air BBO) or nitrogen (N<sub>2</sub> BBO). Binder removal employed a heating rate of 2°C/min up to 550°C, a one hour hold at that temperature and a cooling rate of 2°C/min down to room temperature (25°C).

The AlN powders and their chemical composition are shown in Table III. AlN powders A and B were different lots of powder commercially available from The Dow Chemical Company under the trade designation XUS 35548. AlN powder C was a powder commercially available from The Dow Chemical Company under the trade designation XUS 35544. AlN powders D and E were commercially available from Tokuyama Soda Co., Ltd. as, respectively, grades F and H.

A BN box measuring 7.5 inch by 4.5 inch by 3.5 inch (19.0 cm by 11.4 cm by 8.9 cm) was used as a container to establish a non-reducing environment. The greenware resulting from binder removal was placed in BN setters, one for air BBO and one for N<sub>2</sub> BBO. A one cubic foot (0.028 cubic meter) graphite furnace (Thermal Technology Model 121212G) was used for sintering.

The conditions that were used for sintering are shown in Table IV. Table V shows the results of sintering N<sub>2</sub> BBO greenware. Table VI shows the results of sintering air BBO greenware. Column headings in Tables V and VI, such as A-3 or B-2 refer to the AlN powder type (Table III) before the hyphen and the amount of sintering aid, in wt%, after the hyphen. Two TC values are shown for most sintering runs in Tables V and VI. This reflects measurements made on two different pieces of greenware made from a single admixture and sintered at the same time.

Table IV. Sintering Package Design

Sintering Run	Heating Rate (°C/min)	Soak Temperature (°C)	Soak Time (minutes)	Cooling Rate (°C/min)	Cooling Temperature (°C)	Total Time (hours)
1	1	1825	300	0.5	1600	26
2	3	1862	165	2.8	1400	12.8
3	5	1825	30	5	1200	8.3
4	5	1900	30	5	1600	8.6
5	3	1862	165	2.8	1400	12.8
6	1	1900	300	5	1600	20.9
7	3	1862	329	2.8	1400	16.7
8	5	1900	30	0.5	1200	30.9
9	5	1825	30	0.5	1600	13.7
10	1	1900	30	5	1200	17.8
11	3	1862	1	2.8	1400	11.3
12	3	1862	165	2.8	1157	14.2
13	3	1862	165	0.1	1400	88
14	5	1825	300	5	1600	11.4
15	5	1825	300	0.5	1200	31.6
16	5	1900	300	0.5	1600	21.2
17	3	1862	165	2.8	1643	11.3

Table IV. Sintering Package Design

Sintering Run	Heating Rate (°C/min)	Soak Temperature (°C)	Soak Time (minutes)	Cooling Rate (°C/min)	Cooling Temperature (°C)	Total Time (hours)
18	3	1862	30	2.8	1400	12.8
19	5	1900	300	5	1200	13.3
20	1	1825	30	0.5	1200	35
21	3	1817	165	2.8	1400	13.4
22	0.6	1862	165	2.8	1400	26.8
23	1	1825	300	5	1200	20.7
24	1	1900	30	0.5	1600	25.6
25	3	1908	165	2.8	1400	14.5
26	1	1825	30	5	1600	14.8
27	3	1862	165	5.5	1400	11.4
28	3	1862	165	2.8	1400	12.8
29	5.4	1862	165	2.8	1400	11.2
30	1	1900	300	0.5	1200	43.1

Table V. Measured Thermal Conductivities (W/m·K) for Sintered Parts Prepared From Nitrogen Debindered Greenware

Sintering Run	A-2	B-2	B-3	C-3	D-3	E-3
1	223-231	211-225	200-208	206-220	206	200-205
2	217-218	208-213	208-212	206-211	206	197-198
3	189-193	189-195	192-196	183-184	189	180-182
4	181-181	160-164	180-181	173-174	180	188-189
5	218-223	215-219	213-217	217-218	224	207-214
6	228-238	224-233	221-228	226-231	219	207-214
7	202-208	182-189	203-205	189-194	200	208-208
8	201-202	184-185	204-209	204-207	199	205-208
9	208-210	214-215	208-210	210-213	214	204-206
10	213-225	209-213	205-206	209-212	214	198-198
11	182-186	165-167	181-181	177-181	182	192-195
12	233-233	216-223	218-219	214-222	230	216-219
13	269-274	258-267	274-277	260-270	285	256-263
14	214-221	206-206	208-213	205-205	210	202-199
15	181-200	187-206	212-212	186-194	207	208-208
16	204-208	206-207	201-204	197-200	211	198-199
17	213-217	215-215	209-213	206-209	216	202-204
18	217-220	221-223	212-214	207-209	226	205-205
19	228-231	232-236	221-228	216-220	253	216-217
20	242-245	244-244	245-247	236-236	240	229-229
21	189-195	177-178	187-193	177-182	189	193-198
22	222-231	225-230	222-224	220-222	217	214-215
23	223-223	217-227	216-219	213-217	223	208-208
24	237-238	225-228	221-225	223-224	225	214-222
25	193-196	180-186	199-203	192-193	196	196-202
26	197-203	197-199	198-200	191-193	190	184-185
27	208-210	202-203	208-215	205-206	205	198-199

Table V. Measured Thermal Conductivities (W/m·K) for Sintered Parts Prepared From Nitrogen Debindered Greenware

Sintering Run	A-2	B-2	B-3	C-3	D-3	E-3
28	217-220	202-203	205-207	206-207	203	202-203
29	218-220	200-204	211-217	206-210	203	202-205
30	235-235	225-233	227-228	229-235	235	218-221

Table VI. Measured Thermal conductivities (W/m.K) For Sintered Parts Prepared From Air Debindered Greenware

Sintering Run	A-2	B-2	B-3	C-3	D-3	E-3
1	178-179	158-166	180-185	179-187	182	182-183
2	160-163	153-155	171-172	167-175	164	169-170
3	153-153	134-135	161-164	162-164	161	158-162
4	138-141	125-125	161-161	147-148	148	160-161
5	163-166	154-155	179-181	169-170	175	173-177
6	182-187	169-177	186-189	188-189	183	182-185
7	157-160	144-145	175-179	160-163	167	173-173
8	162-164	152-155	179-182	167-170	168	181-185
9	182-183	159-166	185-194	184-189	182	178-179
10	165-166	153-153	180-183	168-169	171	175-177
11	146-147	120-123	162-163	154-159	159	164-166
12	167-167	156-160	186-188	181-182	168	180-184
13	207-211	198-200	217-217	214-214	218	206-207
14	177-182	162-165	179-182	181-184	183	178-186
15	179-185	169-170	185-189	172-177	175	188-194
16	138-141	125-134	149-152	133-140	131	135-147
17	159-161	148-151	172-177	163-164	162	162-173
18	161-164	154-156	175-176	164-168	164	171-176
19	171-180	165-170	179-181	171-179	193	180-184
20	177-189	178-184	192-193	186-192	180	192-199
21	165-168	140-139	171-174	170-178	177	172-175
22	172-173	160-162	186-187	175-178	175	179-183
23	176-176	166-172	185-190	175-177	189	182-190
24	177-179	175-182	190-191	178-186	176	185-186
25	156-157	145-148	175-179	159-161	163	172-175
26	167-167	149-150	169-175	174-176	177	170-171
27	161-162	153-154	174-182	165-196	173	174-175

Table VI. Measured Thermal conductivities (W/m·K) For Sintered Parts Prepared From Air Debindered Greenware

Sintering Run	A-2	B-2	B-3	C-3	D-3	E-3
28	164-167	156-159	181-181	174-175	177	178-181
29	165-165	153-158	175-181	170-170	170	177-180
30	188-196	181-185	200-200	187-194	195	192-192

The data in Table V show that a  $TC \geq 200 \text{ W/m}^2\text{K}$  was readily attainable under most of the sintering conditions of Table IV. In fact, sintering run 13 provided TC values of 270-285  $\text{W/m}^2\text{K}$  for several powders. Sintering runs 3, 4, 11 and 21 were notable exceptions in that the sintering conditions failed to yield any sintered materials with a  $TC \geq 200 \text{ W/m}^2\text{K}$ .

- 5 Sintering runs 14, 25 and 26, for example, showed that some variability in TC was present even when two pieces of substantially identical greenware were subjected to the same sintering conditions. Sintering runs 2, 7, 8, 10, 15, 16 and 27 showed that variations in powder properties lead to differing results under identical sintering conditions. Based upon the number of sintering run/powder combinations that do provide a  $TC \geq 200 \text{ W/m}^2\text{K}$ , combinations that do  
10 not are readily modified to at least that level by skilled artisans without undue experimentation.

- The data in Table VI show that a  $TC \geq 200 \text{ W/m}^2\text{K}$  was rarely attainable under the conditions shown in Table IV. The success of sintering run 13 suggests that a skilled artisan might make modifications such as an increase in amount of sintering aid or a decrease in  
15 cooling rate, heating rate or both to achieve a  $TC \geq 200 \text{ W/m}^2\text{K}$ . A comparison of run 13 from Table V with run 13 from Table VI suggests that a TC of  $\geq 270 \text{ W/m}^2\text{K}$  may not have been attainable when an air BBO procedure was used with those combinations. However, with elevated levels of  $\text{Y}_2\text{O}_3$  or some other appropriate sintering additive, such TC's may be possible.

- Analysis of all of the sintered bodies, including those having a  $TC > 270 \text{ W/m}^2\text{K}$ ,  
20 by powder X-ray diffraction and electron microscopy revealed the presence of crystalline AlN and secondary boundary phases. The boundary phases contained  $\text{Y}_4\text{Al}_2\text{O}_9$ ,  $\text{YAlO}_3$  or both. The boundary phase was along grain boundaries, at triple points or both. The analysis did not reveal the presence of yttrium nitride.

- Similar results are expected with these powders and the sintering conditions of  
25 Tables I and II. Although some changes in sintering conditions may be required, similar results are also expected with other AlN powders.

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CLAIMS:

1. An improved process for preparing a sintered polycrystalline aluminum nitride body having a thermal conductivity of greater than 200 watts/meter<sup>°K</sup> by heating an admixture of aluminum nitride powder and at least one powdered sintering aid in the presence of nitrogen gas to a sintering temperature, holding the admixture at that  
5 temperature for a period of time sufficient to convert the admixture to a sintered body, and thereafter cooling the body to ambient temperature, characterized by a combination of heating to the sintering temperature at a rate of from greater than 0°C per minute to 6°C per minute, maintaining that temperature for a period of time sufficient to convert the admixture to a sintered body having a density of greater than 95 percent of theoretical density, and  
10 cooling the sintered body in the presence of a vacuum or an inert gas from the sintering temperature to a temperature of 1400°C at a rate of from greater than 0°C/minute to 6°C/minute before cooling the sintered body further to ambient temperature.
2. A process as claimed in Claim 1, wherein the admixture is converted to ceramic greenware prior to sintering.
- 15 3. A process as claimed in Claim 1, wherein cooling is accomplished in the presence of an inert gas that is selected from nitrogen, argon and helium.
4. A process as claimed in Claim 1, wherein the rate of cooling is from 0.1°C/minute to 5.5°C/minute.
5. A process as claimed in any of Claims 1-4, wherein the sintered body is  
20 further present in a non-reducing environment during cooling in the presence of a vacuum or an inert gas.
6. A process as claimed in Claim 5, wherein the non-reducing environment is established by placing the admixture into a crucible fabricated from a non-reducing material prior to sintering and cooling, the non-reducing material being selected from boron nitride, aluminum nitride, molybdenum metal and tungsten metal.  
25
7. A process as claimed in Claim 1, wherein the sintering temperature is within a range of from 1817 to 1908°C.
8. A sintered polycrystalline aluminum nitride body prepared by the process of any of Claims 1-7 and having a microstructure characterized by a crystalline aluminum  
30 nitride phase and secondary grain boundary phases and a thermal conductivity between 270 and 319 watts/meter<sup>°K</sup>.
9. A sintered body as claimed in Claim 8 wherein the grain boundary phases comprise at least one yttrium-aluminate selected from Y<sub>4</sub>Al<sub>2</sub>O<sub>9</sub> and YAlO<sub>3</sub>.
10. A sintered body as claimed in Claim 8 or Claim 9, wherein the grain  
35 boundary phases are located along grain boundaries, at triple points or both.
11. A sintered body as claimed in Claim 10, wherein the thermal conductivity is 274 watts/meter<sup>°K</sup> or greater.

# INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 94/01688

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C04B35/58

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,4 952 535 (G.A. MERKEL) 28 August 1990 see claims 1-15,26,52; figure 2 ---	1-7
A	JOURNAL OF MATERIALS SCIENCE vol. 3, no. 2, June 1992, LONDON, GB pages 93 - 101 XP275448 W.E. LEE ET AL. 'Relation between thermal conductivity, sintering mechanism and microstructure of AlN' see page 94; table II --- -/--	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 94/01688

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>JOURNAL OF THE CERAMIC SOCIETY OF JAPAN vol. 97, no. 12 , December 1989 , TOKYO, JP pages 1486 - 1493 XP140502 M. OKAMOTO ET AL. 'Effect of microstructure on thermal conductivity of AlN ceramics' see figure 1; table 1 -----</p>	1-11

# INTERNATIONAL SEARCH REPORT

information on patent family members

Interr. Application No

PCT/US 94/01688

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4952535	28-08-90	NONE	